

DESCRIPTION

NON-AQUEOUS SECONDARY BATTERY AND
SEPARATOR FOR USE THEREIN

5

Technical Field

The present invention relates to a non-aqueous secondary battery, which produces electromotive force by doping/dedoping of lithium, and to a separator for use
10 therein. In particular, it relates to a battery which ensures safety during periods of overcharging.

Background Art

Non-aqueous secondary batteries, which produce an
15 electromotive force by lithium doping/dedoping, are characterized by having high energy density compared to other types of secondary batteries. Such characteristics meet the demands for lighter weight and miniaturization of portable electronic devices, and such non-aqueous
20 secondary batteries are therefore widely used as power sources for such portable electronic devices as cellular phones and laptop computers.

Common non-aqueous secondary batteries currently employ lithium cobaltate for the positive electrode
25 active material and a carbon material as the negative electrode active material, but research and development is being actively pursued toward achieving even higher performance with such non-aqueous secondary batteries.

One aspect of high performance is increased energy
30 density. One approach that has been studied is the use of lithium nickelate instead of lithium cobaltate as the positive electrode active material. For the negative electrode, silicon-based compounds, tin-based compounds and nitrides have been the focus of research as active
35 substances instead of carbon materials. A technique has been proposed in WO01/22519, and other publications, for exploiting, at the negative electrode, the capacity

component from deposition and dissolution of lithium, in addition to the capacity component due to lithium doping/dedoping according to the conventional viewpoint. The major issue in achieving high energy density is to
5 also ensure safety, but at the current time it is difficult to ensure safety especially during periods of overcharge.

An essential aspect of high performance is improved safety. A variety of technologies have been proposed for
10 improving safety, and one approach has been to look into the use of lithium manganate for the positive electrode active material. Lithium manganate has lower heat release during decomposition by deoxygenation compared to lithium cobaltate, and is therefore an advantageous
15 positive electrode material in terms of ensuring safety. However, since virtually all of the lithium in the positive electrode active material is used during charge-discharge, the amount of lithium stored in the positive electrode active material during full charge is smaller,
20 and therefore the material is disadvantageous for ensuring safety during periods of overcharge by the technique described in WO01/67536. Consequently, ensuring safety during periods of overcharge has been a serious issue.

25 Current non-aqueous secondary batteries employ polyolefin fine porous films with a shutdown function as separators. The shutdown function also effectively works in a comparatively mild non-aqueous secondary battery safety test for external shorts and the like, and can
30 thus contribute to ensuring safety of non-aqueous secondary batteries. However, it is not always effective for ensuring safety during periods of overcharge.

Protective circuits are currently employed in non-aqueous secondary batteries to ensure safety during
35 overcharge. Electronic circuits acting as protective circuits are expected to undergo breakage and are therefore essentially unsafe, and this is currently one

of the major obstacles against achieving high performance in non-aqueous secondary batteries.

The present inventors have proposed, in W001/67536, a new overcharge-preventing function and a separator which performs the function. Overcharge is prevented using a metal lithium species which is deposited on the negative electrode surface during periods of overcharge. A similar invention is also described in Japanese Unexamined Patent Publication No. 2002-42867.

The overcharge-preventing function described in W001/67536 and discovered by the present inventors markedly increases the safety of non-aqueous secondary batteries during periods of overcharge, and employing the function can significantly reduce dependence on protective circuits. However, it has become difficult to apply the overcharge-preventing function discovered by the present inventors, in a simple manner, given the climate of increasing the performance of non-aqueous secondary batteries.

Since approximately half of the lithium in the lithium cobaltate is used for charge-discharge in current non-aqueous secondary batteries employing lithium cobaltate in the positive electrode, about half of the lithium remains in the lithium cobaltate even during full charge. During periods of overcharge, this lithium is released and deposited on the negative electrode surface, and the overcharge-preventing function described in W001/67536 is based on the principle of preventing overcharge using the deposited metal lithium. Consequently, a sufficient amount of metal lithium must be deposited in order to realize the overcharge-preventing function.

With lithium nickelate or lithium manganate recently proposed as positive electrodes, the proportion of lithium in the lithium present which can be used for charge-discharge is greater compared to using the cobaltate and, therefore, the proportion of lithium

remaining in the positive electrode during periods of full charge, which can contribute to the overcharge-preventing function, is smaller. Thus, when lithium nickelate or lithium manganate is used for the positive electrode it has been more difficult, to effectively exhibit the overcharge-preventing function, than when lithium cobaltate is used.

Also, in the case of a non-aqueous battery wherein the capacity component due to deposition and dissolution of lithium at the negative electrode, in addition to the capacity component due to lithium doping/dedoping, is exploited for charge-discharge as described in WO01/22519, a different problem arises when it is attempted to exhibit an overcharge-preventing function. As the overcharge-preventing function is based on the principle of preventing overcharge by using lithium metal which is deposited at the negative electrode, the overcharge-preventing function is exhibited before a full charge can occur in this type of battery, and it thus becomes impossible to accomplish charging as designed (this will hereinafter be referred to as an "insufficient charge phenomenon").

Japanese Unexamined Patent Publication No. 2002-42867 discloses application of the overcharge-preventing function to the battery described in WO01/22519. However, the separator disclosed in Japanese Unexamined Patent Publication No. 2002-42867 is a nonwoven fabric retaining polyvinylidene fluoride (PVdF), and the polyvinylidene fluoride layer is not porous but rather has a dense structure. With this type of separator it is difficult to obtain sufficient rate properties, and it is therefore impractical. The rate properties can be improved by a smaller thickness, but since the PVdF layer itself does not have adequate ion conductivity, the current concentration effect of the nonwoven fabric increases, thereby leading to a notable insufficient charge phenomenon. Consequently, with a separator having

this kind of structure it is extremely difficult to achieve both practical rate properties and an overcharge-preventing function while avoiding the insufficient charge phenomenon.

5

Disclosure of Invention

It is therefore an object of the present invention to provide a construction for a non-aqueous secondary battery such as a battery using lithium nickelate or
10 lithium manganate in the positive electrode or a battery which also exploits the capacity component due to deposition and dissolution of lithium at the negative electrode, wherein an overcharge-preventing function can be effectively exhibited even while higher performance is
15 achieved.

In order to achieve the object stated above, the invention provides a non-aqueous secondary battery which employs a negative electrode in which the negative electrode active material is a material capable of
20 lithium doping/dedoping, a positive electrode in which the positive electrode active material is a lithium-containing transition metal oxide, and a non-aqueous electrolyte solution as the electrolyte solution, wherein

(1) the separator is composed of a porous film made
25 of an organic polymer, which includes a network-like support, and swells in the electrolyte solution and retains the electrolyte solution,

(2) the network-like support has a mean film thickness of 10-30 μm , a basis weight of 6-20 g/m^2 , a
30 Gurley value (JIS P8117) of no greater than 10 sec/100 cc, a McMullin number of no greater than 10 at 25°C and a (McMullin number x film thickness) product of no greater than 200 μm .

(3) the separator has a mean film thickness of 10-35
35 μm , a basis weight of 10-25 g/m^2 and a Gurley value (JIS P8117) of no greater than 60 sec/100 cc, and

(4) the following relationship I:

$$Q_{pr}W_p < q_m + Q_nW_n < 1.3Q_pW_p \quad I$$

is satisfied, wherein the value of the total amount of lithium in the positive electrode active material in terms of electric charge is Q_p (mAh/mg), the amount of lithium utilized for charge-discharge reaction of the lithium in the positive electrode active material in terms of electric charge is Q_{pr} (mAh/mg), the value of the amount of lithium which can be doped in the negative electrode active material in terms of electric charge is Q_n (mAh/mg), the value for the overcharge-preventing function of the separator is q_m (mAh/cm²), the weight of the positive electrode active material is W_p (mg/cm²) and the weight of the negative electrode active material is W_n (mg/cm²).

The invention further provides a non-aqueous secondary battery which employs a negative electrode in which the negative electrode active material is a material capable of lithium doping/dedoping, a positive electrode in which the positive electrode active material is a lithium-containing transition metal oxide, and a non-aqueous electrolyte solution as the electrolyte solution, wherein

(1) the separator is composed of a porous film made of an organic polymer, which includes a network-like support, and swells in the electrolyte solution and retains the electrolyte solution,

(2) the network-like support has a mean film thickness of 10-30 μ m, a basis weight of 6-20 g/m², a Gurley value (JIS P8117) of no greater than 10 sec/100 cc, a McMullin number of no greater than 10 at 25°C and a (McMullin number x mean film thickness) product of no greater than 200 μ m.

(3) the separator has a mean film thickness of 10-35 μ m, a basis weight of 10-25 g/m² and a Gurley value (JIS P8117) exceeding 60 sec/100 cc and no greater than 500

sec/100 cc, and

(4) the following relationship:

$$Q_{pr}W_p < q_m + Q_nW_n < 1.3Q_pW_p \quad I$$

is satisfied, wherein the value of the total amount of
5 lithium in the positive electrode active material in
terms of electric charge is Q_p (mAh/mg), the amount of
lithium utilized for charge-discharge reaction of the
lithium in the positive electrode active material in
terms of electric charge is Q_{pr} (mAh/mg), the value of
10 the amount of lithium which can be doped in the negative
electrode active material in terms of electric charge is
 Q_n (mAh/mg), the value for the overcharge-preventing
function of the separator is q_m (mAh/cm²), the weight of
the positive electrode active material is W_p (mg/cm²) and
15 the weight of the negative electrode active material is
 W_n (mg/cm²).

Further, the invention provides a battery separator
composed of a porous film made of a polymer, which
includes a network-like support, swells in the
20 electrolyte solution and retains the electrolyte
solution, wherein the network-like support has a mean
film thickness of 10-30 μ m, a basis weight of 6-20 g/m², a
Gurley value (JIS P8117) of no greater than 10 sec/100
cc, a McMullin number of no greater than 10 at 25°C and a
25 (McMullin number x mean film thickness) product of no
greater than 200 μ m, and the porous film has a mean film
thickness of 10-35 μ m, a basis weight of 10-25 g/m² and a
Gurley value (JIS P8117) exceeding 60 sec/100 cc and no
greater than 500 sec/100 cc.

30 In other words, the present invention comprises, for
example, the following aspects.

1. A non-aqueous secondary battery which employs a
negative electrode in which the negative electrode active
material is a material capable of lithium
35 doping/dedoping, a positive electrode in which the
positive electrode active material is a lithium-

containing transition metal oxide, and a non-aqueous electrolyte solution as the electrolyte solution, wherein

(1) the separator is composed of a porous film made of a porous polymer, which includes a network-like support, and swells in the electrolyte solution and retains the electrolyte solution,

(2) the network-like support has a mean film thickness of 10-30 μm , a basis weight of 6-20 g/m^2 , a Gurley value (JIS P8117) of no greater than 10 sec/100 cc, a McMullin number of no greater than 10 at 25°C and a (McMullin number x film thickness) product of no greater than 200 μm .

(3) the separator has a mean film thickness of 10-35 μm , a basis weight of 10-25 g/m^2 and a Gurley value (JIS P8117) of no greater than 60 sec/100 cc, and

(4) the following relationship:

$$Q_{pr}W_p < q_m + Q_nW_n < 1.3Q_pW_p \quad I$$

is satisfied, wherein the value of the total amount of lithium in the positive electrode active material in terms of electric charge is Q_p (mAh/mg), the amount of lithium utilized for charge-discharge reaction of the lithium in the positive electrode active material in terms of electric charge is Q_{pr} (mAh/mg), the value of the amount of lithium which can be doped in the negative electrode active material in terms of electric charge is Q_n (mAh/mg), the value for the overcharge-preventing function of the separator is q_m (mAh/cm²), the weight of the positive electrode active material is W_p (mg/cm²) and the weight of the negative electrode active material is W_n (mg/cm²).

2. A battery according to 1. above, wherein $Q_{pr}W_p/Q_nW_n = 0.7-1.05$.

3. A battery according to 1. above, wherein the positive electrode active material is a lithium-containing transition metal oxide represented by LiMO_2 , where M is at least one metal element selected from the

group consisting of cobalt, nickel, manganese, aluminum, iron, titanium and vanadium, and at least 1/3 of the atomic ratio composition of M is cobalt or nickel.

5 4. A battery according to 1. above, wherein the positive electrode active material is a lithium-containing transition metal oxide represented by LiM_2O_4 where M is at least one metal element selected from the group consisting of manganese, magnesium, nickel, cobalt, chromium, copper, iron and boron, and at least 1/3 of the
10 atomic ratio composition of M is manganese.

5. A battery according to 1. above, wherein the positive electrode active material is lithium nickelate (LiNiO_2).

15 6. A battery according to 1. above, wherein the positive electrode active material is lithium manganate (LiMn_2O_4).

7. A battery according to 1. above, wherein the positive electrode active material is composed of lithium manganate (LiMn_2O_4) and lithium nickelate (LiNiO_2).

20 8. A battery according to 1. above, wherein the network-like support is a nonwoven fabric.

9. A battery according to 8. above, wherein the fiber composing the nonwoven fabric is composed of at least one type of high molecular weight polymer selected
25 from the group consisting of polyolefins, polyphenylene sulfide, aromatic polyamides and polyesters.

10. A battery according to 1. above, wherein the network-like support is a cloth.

30 11. A battery according to 10. above, wherein the network-like support is a glass cloth.

12. A battery according to any one of 1. to 11. above, wherein the overcharge-preventing function value q_m of the separator is in the range of 0.1-1.5 mAh/cm^2 .

35 13. A battery according to 12. above, wherein the overcharge-preventing function value q_m of the separator is in the range of 0.1-1.0 mAh/cm^2 .

14. A non-aqueous secondary battery which employs a

negative electrode in which the negative electrode active material is a material capable of lithium doping/dedoping, a positive electrode in which the positive electrode active material is a lithium-containing transition metal oxide, and a non-aqueous electrolyte solution as the electrolyte solution, wherein

(1) the separator is composed of a porous film made of an organic polymer, which includes a network-like support, and swells in the electrolyte solution and retains the electrolyte solution,

(2) the network-like support has a mean film thickness of 10-30 μm , a basis weight of 6-20 g/m^2 , a Gurley value (JIS P8117) of no greater than 10 sec/100 cc, a McMullin number of no greater than 10 at 25°C and a (McMullin number x mean film thickness) product of no greater than 200 μm .

(3) the separator has a mean film thickness of 10-35 μm , a basis weight of 10-25 g/m^2 and a Gurley value (JIS P8117) exceeding 60 sec/100 cc and no greater than 500 sec/100 cc, and

(4) the following relationship:

$$Q_{pr}W_p < q_m + Q_nW_n < 1.3Q_pW_p \quad I$$

is satisfied, wherein the value of the total amount of lithium in the positive electrode active material in terms of electric charge is Q_p (mAh/mg), the amount of lithium utilized for charge-discharge reaction of the lithium in the positive electrode active material in terms of electric charge is Q_{pr} (mAh/mg), the value of the amount of lithium which can be doped in the negative electrode active material in terms of electric charge is Q_n (mAh/mg), the value for the overcharge-preventing function of the separator is q_m (mAh/ cm^2), the weight of the positive electrode active material is W_p (mg/ cm^2) and the weight of the negative electrode active material is W_n (mg/ cm^2).

15. A battery according to 14. above, wherein

$Q_{prWp}/Q_{nWn} = 1.05-4.0$.

5 16. A battery according to 14. above, wherein the positive electrode active material is a lithium-containing transition metal oxide represented by $LiMO_2$, where M is at least one metal element selected from the group consisting of cobalt, nickel, manganese, aluminum, iron, titanium and vanadium, and at least 1/3 of the atomic ratio composition of M is cobalt or nickel.

10 17. A battery according to 14. above, wherein the positive electrode active material is a lithium-containing transition metal oxide represented by LiM_2O_4 where M is at least one metal element selected from the group consisting of manganese, magnesium, nickel, cobalt, chromium, copper, iron and boron, and at least 1/3 of the atomic ratio composition of M is manganese.

15 18. A battery according to 14. above, wherein the positive electrode active material is lithium nickelate ($LiNiO_2$).

20 19. A battery according to 14. above, wherein the positive electrode active material is lithium manganate ($LiMn_2O_4$).

25 20. A battery according to 14. above, wherein the positive electrode active material is composed of lithium manganate ($LiMn_2O_4$) and lithium nickelate ($LiNiO_2$).

30 21. A battery according to 14. above, wherein the network-like support is a nonwoven fabric.

35 22. A battery according to 21. above, wherein the fiber composing the nonwoven fabric is composed of at least one type of high molecular weight polymer selected from the group consisting of polyolefins, polyphenylene sulfide, aromatic polyamides and polyesters.

 23. A battery according to 14. above, wherein the network-like support is a cloth.

 24. A battery according to 23. above, wherein the network-like support is a glass cloth.

 25. A battery according to any one of 14. to 24. above, wherein the overcharge-preventing function value

qm of the separator is in the range of 1.0-5.0 mAh/cm².

26. A battery according to 25. above, wherein the overcharge-preventing function value qm of the separator is in the range of 1.5-3.0 mAh/cm².

5 27. A battery separator composed of a porous film made of a polymer, which includes a network-like support, swells in the electrolyte solution and retains the electrolyte solution, wherein the network-like support has a mean film thickness of 10-30 μm, a basis weight of
10 6-20 g/m², a Gurley value (JIS P8117) of no greater than 10 sec/100 cc, a McMullin number of no greater than 10 at 25°C and a (McMullin number x mean film thickness) product of no greater than 200 μm, and the porous film has a mean
15 film thickness of 10-35 μm, a basis weight of 10-25 g/m² and a Gurley value (JIS P8117) exceeding 60 sec/100 cc and no greater than 500 sec/100 cc.

28. A separator according to 27. above, wherein the network-like support is a nonwoven fabric.

29. A separator according to 28. above, wherein the
20 fiber composing the nonwoven fabric is composed of at least one type of high molecular weight polymer selected from the group consisting of polyolefins, polyphenylene sulfide, aromatic polyamides and polyesters.

30. A separator according to 27. above, wherein the
25 network-like support is a cloth.

31. A separator according to 30. above, wherein the network-like support is a glass cloth.

32. A separator according to 27 above, wherein the
30 organic polymer is polyvinylidene fluoride (PVdF), a PVdF copolymer or a compound composed mainly of PVdF.

Brief Description of the Drawings

Fig. 1 is a reference graph showing voltage change during overcharge of ⊙ in Evaluation 2.

35 Fig. 2 is a reference graph showing voltage change during overcharge of ○ in Evaluation 2.

Fig. 3 is a reference graph showing voltage change during overcharge of x in Evaluation 2.

Best Mode for Carrying Out the Invention

5 Preferred embodiments of the invention will now be described.

Non-aqueous secondary battery 1

The separator used in the non-aqueous secondary battery according to the first embodiment of the invention is composed of a porous film made of an organic polymer which includes a network-like support, and swells in the electrolyte solution and retains it, wherein the network-like support has a mean film thickness of 10-30 μm , a basis weight of 6-20 g/m^2 , a Gurley value (JIS P8117) of no greater than 10 sec/100 cc and a McMullin number of no greater than 10 at 25°C and a (mean film thickness x McMullin number) product of no greater than 200 μm , while the separator has a mean film thickness of 10-35 μm , a basis weight of 10-25 g/m^2 and a Gurley value (JIS P8117) of no greater than 60 sec/100 cc. This type of separator has the overcharge-preventing function described in WO01/67536.

The morphology of the separator is an important factor for exhibiting the overcharge-preventing function, and the Gurley value (JIS P8117) which is an indicator of this factor, is preferably no greater than 60 sec/100 cc. It is more preferably no greater than 30 sec/100 cc. In order to exhibit this range of Gurley value (JIS P8117), it is preferred to use a network-like support having a mean film thickness of 10-30 μm , a basis weight of 6-20 g/m^2 and a Gurley value (JIS P8117) of no greater than 10 sec/100 cc, and a separator having a mean film thickness of 15-35 μm and a basis weight of 10-25 g/m^2 .

Also, the mean film thickness of the separator is preferably smaller in consideration of the energy density of the battery, and from this standpoint it is preferably

no greater than 35 μm , which means that the mean film thickness of the network-like support is preferably no greater than 30 μm . The separator is preferably not too thin from the standpoint of preventing shorts, and is
5 most suitably 11 μm or greater, which means that the mean film thickness of the network-like support is preferably at least 10 μm .

From the standpoint of achieving adequate battery characteristics, the separator must exhibit adequate ion permeability. From this viewpoint, the McMullin number
10 of the network-like support is preferably no greater than 10 and the McMullin number \times mean film thickness is preferably no greater than 200 μm . The McMullin number is an indicator of the ion conductivity, and it is
15 determined by dividing the ion conductivity of the electrolyte solution by the ion conductivity of the network-like support when immersed in the electrolyte solution.

A nonwoven fabric or cloth (textile) may be
20 mentioned as a preferred form of the network-like support, and the mean fiber size of the fiber composing it is preferably no greater than 10 μm and more preferably no greater than 5 μm . Since the overcharge-preventing function arises from the morphology of the
25 separator and is basically independent of the material of which it is composed, there are no particular restrictions on the constituent material.

However, when the network-like support is a nonwoven fabric, the constituent material used may be a
30 polyolefin-based material such as polyethylene or polypropylene, a polyester-based material such as polyethylene terephthalate or polybutylene terephthalate or polyphenylene sulfide, an aromatic polyamide or the like, or a mixture thereof, from the standpoint of small
35 thickness, physical properties and durability. Polyethylene terephthalate or a mixture of polyethylene

terephthalate and a polyolefin-based material is preferred.

5 The nonwoven fabric may be produced by a publicly known process. As examples there may be mentioned dry processes, spun bond processes, water needle processes, spun lace processes, wet sheeting processes, melt blow processes and the like. A wet sheeting process is particularly preferred in order to obtain a uniform, thin nonwoven fabric.

10 When the network-like support is a cloth (textile), a glass cloth is preferably used from the viewpoint of low thickness. An fiber-opened glass cloth is particularly preferred. The method for fiber-opening of the glass cloth is preferably a publicly known method
15 such as ultrasonic treatment.

 Using a glass cloth is preferred from the standpoint of obtaining a separator with higher mechanical properties and better handling properties compared to a nonwoven fabric. When the battery element is to be wound
20 for application to a flat-molded battery (for example, a square cell), a glass cloth is most preferably used because of its high perforation strength and resistance to compression. It is also preferred from the standpoint of high thermal dimensional stability, its ability to
25 prevent internal shorting by contact between the positive and negative electrodes even when the battery is exposed to high temperature, and safety. A glass cloth is also preferred from the viewpoint of high chemical stability and durability.

30 The organic polymer used for the invention which swells in the electrolyte solution and retains it is not particularly restricted and, for example, there may be mentioned polyvinylidene fluoride (PVdF), PVdF
 copolymers, polyacrylonitrile (PAN), polyethylene oxide
35 (PEO), polymethyl methacrylate (PMMA) and the like, while mixtures of these may also be used. Organic polymers composed mainly of PVdF are particularly preferred among

these from the standpoint of film formability and oxidation-reduction resistance. As organic polymers composed mainly of PVdF there may be mentioned copolymers such as hexafluoropropylene (HFP),

5 chlorotrifluoroethylene (CTFE), perfluoromethylvinyl ether (PFMV) and the like. The molecular weight of such copolymers is preferably 100,000 to 1 million, as the weight-average molecular weight (Mw). The copolymer composition is most preferably:

10 VdF/HFP/CTFE

HFP = 2-8 wt%

CTFE = 1-6 wt%,

from the standpoint of heat resistance and adhesion with the electrodes.

15 There are no particular restrictions on the process for producing the separator, and for example, it may be produced by a wet film-forming process wherein a dope comprising the organic polymer dissolved in an organic solvent is impregnated into the nonwoven fabric, and the
20 fabric is immersed in a solidifying bath (a mixture of the dope solvent and water) and then washed with water and dried. Here, a phase separating agent which is a weak solvent for the polymer may be added to the dope, or the composition of the solidifying bath adjusted, to
25 control the morphology of the organic polymer layer of the separator. By placing both sides in the solidifying bath in contact with the solidifying bath so that solidification of both sides occurs at the same rate, it is possible to easily control the morphology of the
30 separator.

However, an overcharge-preventing function cannot be reliably obtained merely by using the separator described above. Because the overcharge-preventing function described in WO01/67536 is exhibited via the lithium
35 species deposited on the surface of the negative electrode during periods of overcharge, it is not exhibited in principle unless the total amount of lithium

in the positive electrode is greater than the amount of lithium which can be doped into the negative electrode, as described in the publication; however, a constant amount of lithium must be present between the negative and positive electrodes in order to exhibit this function, and therefore the battery having the function must be designed with the amount of lithium in mind. Specifically, an overcharge-preventing function can be reliably exhibited by adjusting each of the amounts so that the following relationship I:

$$Q_{pr}W_p < q_m + Q_nW_n < 1.3Q_pW_p \quad I$$

is satisfied, wherein the value of the total amount of lithium in the positive electrode active material in terms of electric charge is Q_p (mAh/mg), the amount of lithium utilized for charge-discharge reaction of the lithium in the positive electrode active material in terms of electric charge is Q_{pr} (mAh/mg), the value of the amount of lithium which can be doped in the negative electrode active material in terms of electric charge is Q_n (mAh/mg), the value for the overcharge-preventing function of the separator is q_m (mAh/cm²), the weight of the positive electrode active material is W_p (mg/cm²) and the weight of the negative electrode active material is W_n (mg/cm²).

The balance of capacity of the positive and negative electrodes and the design of the separator are important for the non-aqueous secondary battery of the invention, and if the non-aqueous secondary battery is designed so as to satisfy inequality I above, a cell will be obtained having an effective overcharge-preventing function and no insufficient charge phenomenon. The relationship is more preferably $Q_{pr}W_p \leq Q_nW_n$ in consideration of the cycle characteristic. Even more preferably, the relationship $q_m + Q_nW_n \leq Q_pW_p$ is satisfied. If this condition is satisfied, the overcharge-preventing function will be more reliably exhibited, the battery voltage will not exceed 5 V, decomposition of the electrolyte solution can

be dramatically prevented, and the overcharged cell will be reusable. In contrast, in the range of $Q_p W_p < q_m + Q_n W_n < 1.3 Q_p W_p$, the effect of the overcharge-preventing function is insufficient and decomposition reaction of the electrolyte solution proceeds; nevertheless, since the decomposition reaction of the electrolyte solution is significantly inhibited, an effect will be exhibited for ensuring safety during periods of overcharge. However, if $q_m + Q_n W_n$ is greater than $1.3 Q_p W_p$, virtually no effect of the overcharge-preventing function will be exhibited.

Q_p is determined by calculation from charge-discharge measurement and positive electrode active material composition analysis for an electrochemical cell employing the positive electrode as the working electrode and lithium metal as the counter electrode and reference electrode. When determined by calculation, however, Q_p represents the total amount of lithium, among the lithium in the positive electrode, which can dissociate from the positive electrode during the electrode reaction (electron transfer reaction), and therefore the electron source limit capacity must also be considered. For example, lithium manganate releases lithium ion by the driving force of Mn^{3+}/Mn^{4+} redox, and therefore the Q_p of $Li_{1.135}Mn_{1.875}O_4$ is 9.6×10^{-2} (mAh/mg).

Q_{pr} may be determined by charge-discharge measurement for an electrochemical cell employing the positive electrode as the working electrode and lithium metal as the counter electrode and reference electrode. In this measurement, the charge termination voltage is a voltage of 0.05 V higher than the charge termination voltage set for the non-aqueous secondary battery of the invention, and Q_{pr} may be determined from the initial charging capacity at constant current, constant voltage charge, up to this voltage. That is, the weight of the positive electrode active material (the lithium-containing transition metal oxide) in the positive electrode used for the measurement is recorded

beforehand, and the obtained initial charging capacity is divided by the active substance weight to determine Q_{pr} . Here, a lower charge current density is preferred, and according to the invention the measurement is carried out at 1 mA/cm² or lower.

Q_n may be determined by charge-discharge measurement for an electrochemical cell employing the negative electrode as the working electrode and lithium metal as the counter electrode and reference electrode. The condition for this measurement is 0 V cutoff constant current charging, and Q_n may be determined from the initial charging capacity obtained by this measurement. That is, the weight of the negative electrode active material (material capable of lithium doping-dedoping) in the negative electrode used for the measurement is recorded beforehand, and the obtained initial charging capacity is divided by the active substance weight to determine Q_{pr} . Here, the charge current density is 0.1 mA/cm².

In the electrochemical cell described above, the electrolyte solution used may be a non-aqueous electrolyte solution ordinarily employed for a lithium ion secondary battery.

W_p and W_n may be determined by a method of weight measurement after separating the binder or the conductive aid and the collector from the positive and negative electrodes, or a method of analyzing the composition of the electrodes.

The value of q_m as the overcharge-preventing function property of the separator is the amount of lithium present between the negative and positive electrodes required to exhibit an overcharge-preventing function, and it is a characteristic value of the separator. The value of q_m may be measured as follows. It may be measured using an electrochemical cell (for example, a coin cell) comprising a positive electrode/separator/copper foil laminate, with the

electrolyte solution used being a non-aqueous electrolyte solution commonly used for lithium ion secondary batteries. The metal foil used for lamination in the cell does not necessarily have to be a copper foil, and the foil may be a metal which is stable even at the oxidation-reduction potential for lithium deposition and which does not have intercalated lithium (for example, SUS or the like). The value of q_m may be determined by passing a current through the cell to deposit lithium metal on the copper foil, measuring the charge quantity at which voltage drop, voltage oscillation or voltage increase ceases, and dividing this by the electrode area. The current density for the measurement is preferably the actually employed charging current density, and generally 2-4 mA/cm² is suitable. The voltage sampling time during measurement is preferably no longer than 30 seconds.

As the non-aqueous secondary battery of the invention employs the aforementioned separator which must be designed so as to satisfy inequality I above, the positive electrode active material used may be any publicly known lithium-containing transition metal oxide. That is, lithium cobaltate, lithium nickelate, lithium manganate or the like may be used. Naturally, different element-substituted lithium cobaltate, lithium nickelate and lithium manganate may also be used so long as the concept described above is maintained. As different element-substituted compounds there may be mentioned lithium-containing transition metal oxides represented by LiMO_2 wherein at least 1/3 of the composition of M is cobalt or nickel, or lithium-containing transition metal oxides represented by LiM_2O_4 wherein at least 1/3 of the composition of M is manganese. Specifically, for $\text{Li}(\text{M}_1x_1\text{M}_2x_2\text{M}_3x_3 \dots)\text{O}_2$ ($\text{M}_1 = \text{Co}$ or Ni , $\text{M}_2, \text{M}_3 \dots$ are other elements), $x_1 + x_2 + x_3 \dots = 1$, $x_1 > 1/3$, and as different elements ($\text{M}_2, \text{M}_3 \dots$) there may be mentioned manganese, aluminum, iron, titanium and vanadium. When $\text{M}_1 = \text{Ni}$, cobalt may be added as a different element, and

when $M_1 = \text{Co}$, nickel may be added as a different element.
For $\text{Li}(M_1x_1M_2x_2M_3x_3 \dots)_2\text{O}_4$ ($M_1 = \text{Mn}$, M_2 , $M_3 \dots$ are other
elements), $x_1 + x_2 + x_3 \dots = 1$, $x_1 > 1/3$, and as
different elements (M_2 , $M_3 \dots$) there may be mentioned
5 magnesium, cobalt, nickel, chromium, copper, iron and
boron.

The non-aqueous secondary battery of the invention
exhibits a particularly notable effect when the positive
electrode active material is lithium manganate or lithium
10 nickelate. A mixture of these may also be used. Lithium
nickelate is generally represented by LiNiO_2 , and lithium
manganate is generally represented by LiMn_2O_4 . However,
as mentioned above, these compounds substituted with
different elements may also be included if within the
15 scope of the concept of the invention.

The following reason is thought to explain why a
particularly notable effect is exhibited when the
construction of the non-aqueous secondary battery of the
invention uses lithium manganate or lithium nickelate as
20 the positive electrode active material. Specifically, it
is currently common to use lithium cobaltate (LiCoO_2) as
the positive electrode and a graphite-based material as
the negative electrode, for a lithium ion secondary
battery system used at a charging voltage of 4.2 V.
25 Since the Q_p value of lithium cobaltate is 0.278 mAh/mg
and the Q_{pr} is about 0.16 mAh/mg, the difference $Q_p - Q_{pr} =$
0.118 mAh/mg. In contrast, $Q_p - Q_{pr}$ is 0.028 mAh/mg with
lithium manganate (LiMn_2O_4) and 0.074 mAh/mg with lithium
nickelate (LiNiO_2) under comparable conditions. A higher
30 $Q_p - Q_{pr}$ obviously facilitates establishment of inequality
I above. Consequently, when lithium cobaltate is used as
the positive electrode active material, it has been
possible to obtain an overcharge-preventing function
simply by using the separator of WO01/67536 as the
35 separator in a conventional battery design. However,
since $Q_p - Q_{pr}$ is smaller with lithium nickelate or lithium
manganate, the electrode and separator must be selected

for inequality I to be satisfied, unlike in the case of lithium cobaltate.

5 Since no overcharge-preventing function is exhibited with current lithium ion secondary batteries employing polyolefin fine porous films as separators, deposition of lithium species on the surface of the negative electrode is undesirable, and therefore such batteries are usually designed with Q_nW_n slightly higher than $Q_{pr}W_p$ in order to minimize deposition of lithium species. This is also
10 undesirable for the overcharge-preventing function, but this has not been a problem with lithium cobaltate which has a large Q_p-Q_{pr} ; however, when lithium manganate or lithium nickelate with a small Q_p-Q_{pr} value is used as the positive electrode active material, this can be a
15 factor preventing effective exhibition of the overcharge-preventing function.

In the case of lithium nickelate, design is facilitated due to the relatively large Q_p-Q_{pr} value, but lithium manganate results in a lower degree of design
20 freedom because of the exceedingly small value. In such cases, it is effective to use it in combination with lithium nickelate.

Addition of lithium cobaltate which has a large Q_p-Q_{pr} value is also effective for satisfying inequality I, and such an addition does not fall outside of the concept
25 of the invention.

A cell design with a low established charging voltage is one means for increasing the Q_p-Q_{pr} value. Specifically, Q_p-Q_{pr} can be significantly increased by
30 changing the currently common 4.2 V charging specification to a 4.1 V charging specification. Q_nW_n can also be reduced in such cases. This obviously facilitates establishment of inequality I, thereby making it easier to achieve an overcharge-preventing function.

35 Reducing the q_m value is also important for establishing inequality I and obtaining an overcharge-preventing function. Specifically, a range of 0.1-1.5

mAh/cm² is preferred, with the range of 0.1-1.0 mAh/cm² being more preferred. A value of less than 0.1 mAh/cm² is not preferred as it tends to result in a poor state of charge. The qm value is dependent on the morphology of the separator, and can be controlled by not only the basis weight or film thickness, but also the separator production conditions and the fiber size of the nonwoven fabric. There is a particularly good correlation with the Gurley value (JIS P8117) and, from this viewpoint, it is preferably no greater than 60 sec/100 cc and especially no greater than 30 sec/100 cc.

In a non-aqueous secondary battery according to the first embodiment of the invention, the range of $Q_{prWp}/Q_{nWn} = 0.7-1.05$ is preferred and the range of $Q_{prWp}/Q_{nWn} = 0.9-1.0$ is more preferred, from the standpoint of avoiding the insufficient charge phenomenon and cycle characteristic during the initial charging period.

The negative electrode and positive electrode used in the non-aqueous secondary battery of the invention in most cases are each composed of a mixture layer comprising the active substance and a binder polymer binding it and retaining the electrolyte solution, and a collector. A conductive aid may also be included in the mixture layer.

The negative electrode active material may be any material capable of reversible doping/dedoping of lithium, and there may be mentioned carbon-based materials, metal oxides such as SiO_x ($0 < x < 2$), $SnSiO_3$ and SnO_2 , metal compounds comprising elements such as Si, Sn, Mg, Cu, Pb, Cd and the like, such as Mg_2Si or SiF_4 , lithium nitrides such as Li_3N , Li_7MnN_4 , Li_3FeN_2 or $Li_{2.6}Co_{0.4}N$, antimony compounds such as $CoSb_3$ or Ni_2MnSb , and high molecular compounds such as polyacene, any of which may be used alone or in mixtures of two or more. Carbon-based materials have low charge-discharge potential close to lithium metal, and therefore

facilitate high energy densification and permit a satisfactory cycle characteristic to be achieved. As carbon-based materials there may be mentioned polyacrylonitrile, phenol resins, phenol-novolac resins, fired organic polymers such as cellulose, fired coke or pitch, artificial graphite, natural graphite, and the like. Graphite is preferred among such carbon-based materials because of the large number of electrochemical equivalents. Non-graphitizing carbon is preferred because it can yield a satisfactory cycle property. Here, the content of the non-graphitizing carbon is preferably 3-60% with respect to the total weight of the negative electrode material. From the standpoint of achieving high energy densification, a compound containing Si is preferably included. The content of the Si-containing compound in the negative electrode mixture layer is preferably 1-50% with respect to the total weight of the negative material.

In order to achieve a satisfactory cycle characteristic for the non-aqueous secondary battery, the specific surface area of the negative electrode material is preferably no greater than $5.0 \text{ m}^2/\text{g}$. The packing density of the negative electrode material in the negative electrode mixture layer is preferably at least 40% of the true density of the negative electrode material.

The positive electrode active material may be a lithium-containing transition metal oxide which is typically lithium cobaltate, lithium nickelate or lithium manganate, and this is particularly preferred when lithium nickelate or lithium manganate, or a mixture thereof, is used as described above. A different element-substituted compound is also contained in the negative electrode active material in a range which does not fall outside of the concept of the invention. From the standpoint of battery safety, LiFePO_4 having an olivine structure is preferably added, and this does not

fall outside of the concept of the invention.

Such lithium complex oxides are prepared, for example, by mixing a lithium carbonate, nitrate, oxide or hydroxide with a transition metal carbonate, nitrate, oxide or hydroxide to a prescribed composition, pulverizing the mixture and then firing it at a temperature in the range of 600-1000°C in an oxygen atmosphere.

The powder particle size of the positive electrode active material is preferably specified by a 50% cumulative size of 3-35 μm , a 10% cumulative size of 1-20 μm and a 90% cumulative size of 6-50 μm , and the specific surface area of the positive electrode active material is preferably specified as 0.1-2 m^2/g . Satisfying these conditions increases the possibility of avoiding higher internal resistance or the risk of thermal runaway of the battery.

The positive electrode mixture layer may further comprise a metal carbonate such as lithium carbonate (Li_2CO_3). Including such a metal carbonate is preferred to allow further improvement in the cycle characteristic. This is believed to result from partial decomposition of the metal carbonate at the positive electrode and formation of a stable coating at the negative electrode.

The binder polymer used is preferably polyvinylidene fluoride (PVdF) or a PVdF copolymer resin which may be a copolymer of PVdF with hexafluoropropylene (HFP), perfluoromethylvinyl ether (PFMV), a fluorine resin such as polytetrafluoroethylene or fluororubber, a polyimide resin, or the like. These may be used alone or in combinations of two or more. For the negative electrode there is preferably used a polymer having a diene structure such as polybutadiene, butadiene-acrylonitrile copolymer, styrene-butadiene copolymer or polyisoprene, from the standpoint of adjustment. However, when a polymer with a diene structure is used as the binder, it

is preferred to use a thickening agent in combination therewith. Suitable thickening agents include carboxymethylcellulose derivatives, and specifically there may be mentioned alkali salts and ammonium salts of carboxymethylcellulose. These binder polymers are preferably combined in a range of 3-30 wt% with respect to the weight of the positive electrode active material.

Acetylene black or the like is preferably used as the conductive aid. Conductive fiber materials composed of carbon, copper, nickel or the like having a mean fiber size of about 5-100 nm are also preferred from the standpoint of obtaining a satisfactory cycle characteristic. The contents of these conductive aids are preferably in the range of 0-45 wt% with respect to the positive electrode active material.

For the collector, a material with excellent oxidation resistance is preferably used in the positive electrode and a material with excellent reduction resistance is preferably used in the negative electrode. Specifically, there may be mentioned aluminum, stainless steel or the like as the positive electrode collector, and copper, nickel, stainless steel or the like as the negative electrode collector. The collector may be used in the form of a foil or mesh. In particular, an aluminum foil is preferred as the positive electrode collector and a copper foil is preferred as the negative electrode collector.

The method employed for fabricating the electrode described above is not particularly restricted and may be a publicly known method.

The non-aqueous secondary battery of the invention may employ a solution of a lithium salt in a non-aqueous solvent commonly used for lithium ion secondary batteries.

As specific non-aqueous solvents there may be mentioned propylene carbonate (PC), ethylene carbonate (EC), butylene carbonate (BC), vinylene carbonate (VC),

dimethyl carbonate (DMC), diethyl carbonate (DEC),
methylethyl carbonate (EMC), methylpropyl carbonate, 1,2-
dimethoxyethane (DME), 1,2-diethoxyethane (DEE), γ -
butyrolactone (γ -BL), γ -valerolactone (γ -VL),
5 acetonitrile, methoxyacetonitrile, glutaronitrile,
adiponitrile, 3-methoxypropyronitrile, N,N-
dimethylformamide, N-methylpyrrolidine, N-
methyloxazolidinone, N,N-dimethylimidazolidine,
10 nitromethane, nitroethane, sulfolane, dimethyl sulfoxide,
trimethyl phosphate, phosphazine-based compounds and the
like. Some of the hydroxyl groups of these compounds may
also be replaced with fluorine.

The non-aqueous solvent may be used alone or in a
combination of two or more. These non-aqueous solvents
15 preferably have intrinsic viscosities of no greater than
10.0 mPa·s at 25°C.

Particularly preferred for use are one or more
solvents selected from among PC, EC, γ -BL, DMC, DEC, MEC
and DME. The solvent used also preferably contains at
20 least one from among EC and PC, for a more notably
improved cycle characteristic. A mixture of EC and PC is
especially preferred since it will allow the cycle
characteristic to be even further improved.

However, when graphite is used as the negative
25 electrode, the concentration of PC in the non-aqueous
solvent is preferably less than 30 wt%. Since PC has
relatively high reactivity for graphite, an excessively
high PC concentration can result in inferior properties.
When the non-aqueous solvent contains EC and PC, the
30 mixing weight ratio of EC with respect to PC (EC/PC) in
the non-aqueous solvent is preferably at least 0.5.

The non-aqueous solvent preferably contains at least
one chain carbonic acid ester such as DEC, DMC, EMC or
methylpropyl carbonate, in order to further improve the
35 cycle characteristic.

The non-aqueous solvent more preferably contains at

least one from among 2,4-difluoroanisol (DFA) and
vinylene carbonate (VC). DFA can improve the discharge
capacity, while VC can improve the cycle characteristic.
A mixture of these is preferably used in order to improve
5 both the discharge capacity and the cycle characteristic.

The concentration of DFA in the non-aqueous solvent
is preferably no greater than, for example, 15 wt%. If
the concentration is too high, improvement in the
discharge capacity may be insufficient. The
10 concentration of VC in the non-aqueous solvent is
preferably no greater than, for example, 15 wt%. If the
concentration is too high, the improvement in the cycle
characteristic may be insufficient.

Addition of a pyrocarbonate compound such as
15 dimethyl dicarbonate, a disulfide compound, a compound
having a sulfite structure such as ethylene sulfite, a
compound having a CSC structure such as 1-benzothiophene,
a compound having a NCON structure such as 1,3-dimethyl-
2-imidazolidinone, a compound having an OCON structure
20 such as 3-methyl-2-oxazolidinone, a compound having a
OCOO structure such as γ -BL, or vinyl ethylenecarbonate,
divinyl ethylenecarbonate or the like to the electrolyte
solution is preferred from the standpoint of improving
the cycle characteristic or storage properties and
25 increasing the reliability of the battery. These
compounds may be used alone or in combinations of two or
more.

Examples of suitable lithium salts include LiPF_6 ,
 LiBF_4 , LiAsF_6 , LiClO_4 , $\text{LiB}(\text{C}_6\text{H}_5)_4$, LiCH_3SO_3 , LiCF_3SO_3 ,
30 $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, LiAlCl_4 , LiSiF_6 , $\text{Li}[(\text{OCO})_2]_2\text{B}$,
 LiCl and LiBr , and any one or mixtures of two or more of
which may be used. LiPF_6 is preferred among these in
order to obtain high ion conductivity while further
improving the cycle characteristic. There is no
35 particular restriction on the concentration of the
lithium salt in the non-aqueous solvent, but it is
preferably in the range of 0.1-5.0 mol/dm³ and more

preferably in the range of 0.5-3.0 mol/dm³. It is possible to increase the ion conductivity of the electrolyte solution in this concentration range.

The shape of the non-aqueous secondary battery of the invention may be any commonly used shape such as cylindrical, square, button-shaped, film-sheathed or the like. In the case of a cylindrical or square metal can sheath type, the metal can may be made of stainless steel, aluminum or the like. In the case of a film sheath, an aluminum laminate film may be used. According to the invention, the separator is most preferably a film sheath in order to result in a satisfactory electrolyte solution storage property and adhesion with the electrodes.

The charging method for the battery will generally be constant current or constant voltage charging. However, during the period of initial charging, these methods may result in abnormal current crowding, or an insufficient charge phenomenon even if inequality I above is satisfied (the insufficient charge phenomenon during the period of initial charging will hereinafter be referred to as "initial insufficient charge phenomenon"). In order to avoid this, the method may involve initial charging at a low rate. When initial charging is carried out at a higher rate, a procedure of carrying out charging up to an appropriate charging rate followed by aging is effective for avoiding insufficient charge. Gas release is preferably accomplished during such aging.

Non-aqueous secondary battery 2

When considering further increased capacity of the non-aqueous secondary battery of the invention, a negative electrode may be employed which includes the capacity component from deposition and dissolution of lithium in addition to the capacity component due to lithium doping/dedoping into the negative electrode active material. The separator used in the non-aqueous secondary battery according to the second embodiment of

the invention is composed of a porous film made of an organic polymer, which includes a network-like support, and swells in the electrolyte solution and retains it, wherein the network-like support has a mean film
5 thickness of 10-30 μm , a basis weight of 6-20 g/m^2 , a Gurley value (JIS P8117) of no greater than 10 sec/100 cc and a McMullin number of no greater than 10 at 25°C and a (mean film thickness x McMullin number) product of no greater than 200 μm , while the separator has a mean film
10 thickness of 10-35 μm , a basis weight of 10-25 g/m^2 and a Gurley value (JIS P8117) of greater than 60 sec/100 cc and no greater than 500 sec/100 cc.

A separator having a Gurley value (JIS P8117) of 60 sec/100 cc or smaller has a small q_m and, as such a
15 battery exhibits a small $Q_n W_n$ value, it is difficult to satisfy the condition $Q_{pr} W_p < q_m + Q_n W_n$ in the aforementioned inequality I. The battery will therefore be prone to the insufficient charge phenomenon. Therefore, a relatively large q_m is preferred in such a
20 battery, and preferably the separator used has a Gurley value (JIS P8117) of greater than 60 sec/100 cc and no greater than 500 sec/100 cc. It is more preferably greater than 60 sec/100 cc and no greater than 200 sec/100 cc, particularly greater than 60 sec/100 cc and
25 no greater than 150 sec/100 cc, and especially at least 80 sec/100cc and no greater than 150 sec/100 cc. The specific q_m value is preferably in the range of 1.0-5.0 mAh/cm^2 and more preferably in the range of 1.5-3.0 mAh/cm^2 .

30 Control of the Gurley value (JIS P8117) of the separator to within these ranges is accomplished by controlling the morphology of the network-like support or the layer comprising the organic polymer. Control of the morphology of the organic polymer layer is especially
35 important, and this can be easily accomplished by changing the film-forming conditions in the wet film-

forming method used to produce the separator.

5 The rest of the construction of the separator used in this non-aqueous secondary battery is basically the same as the separator used in the non-aqueous secondary battery according to the first embodiment described above.

10 This non-aqueous secondary battery and the non-aqueous secondary battery according to the first embodiment described above are identical in the fundamental concept of satisfying inequality I, differing only in the separator explained above. Using this type of separator provides the following two advantages.

15 In the non-aqueous secondary battery of the first embodiment, the insufficient charge phenomenon occurs relatively easily during the initial charging period and the initial charging is therefore difficult. However, the non-aqueous secondary battery of this second embodiment has the advantage of facilitating the initial charging.

20 This non-aqueous secondary battery permits a design with high capacity, and employs a negative electrode which includes the capacity component from deposition and dissolution of lithium in addition to the capacity component due to lithium doping/dedoping into the negative electrode active material. That is, the amount of lithium utilized for a charge-discharge reaction of the lithium at the positive electrode in terms of electric charge (Q_{prWp}) is greater than the amount of lithium which can be doped in the negative electrode active material of the negative electrode in terms of electric charge (Q_{nWn}). In this type of non-aqueous secondary battery, a range of $Q_{prWp}/Q_{nWn} = 1.05-4.0$ is preferred from the standpoint of the cycle characteristic. If this ratio exceeds 4.0, the cycle characteristic will be notably impaired.

35 When the aforementioned high capacity design (specifically, $Q_{prWp}/Q_{nWn} = 1.05-4.0$) is employed in this

second embodiment of a non-aqueous secondary battery,
observation of the negative electrode in the fully
charged state reveals silver coloring due to a plating of
lithium metal. Also, measurement of the negative
5 electrode in the fully charged state by ^7Li multinuclear
magnetic resonance spectroscopy results in observation of
both a lithium metal peak and a lithium ion peak. In
addition, differential scanning calorimetry (DSC)
analysis yields an endothermic peak due to melting of
10 lithium metal, while Raman scattering spectroscopy
reveals a scattering peak in the wavelength region of
1800-1900 cm^{-1} .

The rest of the construction of this non-aqueous
secondary battery is the same as the non-aqueous
15 secondary battery of the first embodiment described
above.

The charging method for this non-aqueous secondary
battery may also be ordinary constant current or constant
voltage charging. In particular, when employing a high
20 capacity design (specifically, $Q_{\text{prWp}}/Q_{\text{nWn}} = 1.05-4.0$), a
charging current of no greater than 1.5 C is preferred to
avoid impairing the cycle characteristic. Also, charging
at no greater than 0.8 C is preferred for the initial
charging during production of the battery, as this
25 condition will prevent subsequent impairment of the cycle
characteristic. With a high capacity design
(specifically, $Q_{\text{prWp}}/Q_{\text{nWn}} = 1.05-4.0$) for this non-
aqueous secondary battery, the insufficient charge
phenomenon may occur due to abnormal current crowding
30 during the period of initial charging even if inequality
I is satisfied, but the aforementioned initial charging
conditions can avoid the insufficient charge phenomenon
during the initial charging period. In order to avoid
the initial insufficient charge phenomenon, it is
35 preferred to carry out a procedure of charging up to an
appropriate charging rate for aging, and a step for
release of generated gas is also preferably carried out

during the initial charging period. Another suitable method is charging by application of an intermittent voltage with an off-duty period of at least 1 ms (millisecond), to allow a satisfactory cycle characteristic to be achieved. This procedure may be suitably employed for the initial charging or for subsequent charging.

The present invention will now be more fully explained in by examples, with the understanding that these examples are in no way limitative on the invention.

Experimental Example 1

Experimental Example 1 was carried out to examine inequality I in detail.

Separator

Measuring method for McMullin number

An electrolyte solution-impregnated nonwoven fabric was sandwiched between 20 mm ϕ SUS electrodes, the alternating current impedance was measured at 10 kHz, and the ion conductivity was calculated. The McMullin number was determined by dividing this value into the ion conductivity of the electrolyte solution alone as measured with a separate conductivity meter. Here, the measuring temperature was 25°C and the electrolyte solution was 1 mol/dm³ LiBF₄EC/PC (1/1 weight ratio).

Measuring method for qm

The method described below for electrode fabrication was used to fabricate a positive electrode comprising aluminum foil as the collector, having a composition of LiCoO₂:PVdF:acetylene black = 89.5:6:4.5 (weight ratio), with a basis weight of 23 mg/cm² (electrode layer) and a density of 2.8 g/m³ (electrode layer). The positive electrode (ϕ 14 mm), a copper foil (ϕ 15 mm) and a separator (ϕ 16 mm) were used to produce a coin cell (CR2032) comprising the positive electrode/separator/copper foil (effective electrode area: 1.54 cm²). For the electrolyte solution there was used 1 mol/dm³ LiPF₆EC/EMC (3/7 weight

ratio). The cell was electrified at a current density of 3 mA/cm² for electrodeposition of lithium metal on the copper foil. The electric charge at which termination of voltage drop, voltage oscillation or voltage rise began was measured, and this was divided by the electrode area to determine the qm value.

Fabrication of separator

Separator A

A PET staple fiber with a fiber size of 0.11 dtex (product of Teijin Co., Ltd.) was used as the main fiber. A PET staple fiber with a fiber size of 1.21 dtex (product of Teijin Co., Ltd.) was used as the binder fiber. The main fiber and binder fiber were mixed in a proportion of 6:4, and a nonwoven fabric with a mean film thickness of 17 μm and a basis weight of 14 g/m² was obtained by a wet sheeting method. The McMullin number of the nonwoven fabric was 4.2, and the (McMullin number x mean film thickness) product was 71.4. The Gurley value (JIS P8117) was 0.1 sec/100 cc or smaller.

A PVdF copolymer having a composition of vinylidene fluoride:hexafluoropropylene:chlorotrifluoroethylene = 92.2:4.4:3.4 (weight ratio) and a weight average molecular weight Mw of 410,000 was dissolved in a 6/4 (weight ratio) mixed solvent of N,N-dimethylacetamide (DMAc) and polypropylene glycol with an average molecular weight of 400 (PPG-400), to a copolymer concentration of 12 wt% at 60°C, to prepare a film-forming dope. The aforementioned nonwoven fabric was dip coated in the obtained dope, and then immersed in an aqueous solution with a 40 wt% solvent concentration for solidification and washed with water and dried to obtain a nonwoven fabric-reinforced separator. The mean film thickness of the separator was 29 μm and the basis weight was 21 g/m². The Gurley value (JIS P8117) of this separator was 29 sec/100 cc. The qm value was 1.15 mAh/cm².

Separator B

A PET staple fiber with a fiber size of 0.11 dtex (product of Teijin Co., Ltd.) was used as the main fiber. A core-sheath staple fiber with a fiber size of 0.77 dtex, comprising PP as the core section and PE as the sheath section (product of Daiwabo Co., Ltd.) was used as the binder fiber. The main fiber and binder fiber were mixed in a proportion of 1:1, and a nonwoven fabric with a mean film thickness of 20 μm and a basis weight of 12 g/m^2 was obtained by a wet sheeting method. The McMullin number of the nonwoven fabric was 9.6, and the (McMullin number \times mean film thickness) product was 192. The Gurley value (JIS P8117) was 0.1 sec/100 cc or smaller.

A PVdF copolymer having a composition of vinylidene fluoride:hexafluoropropylene:chlorotrifluoroethylene = 92.2:4.5:3.5 (weight ratio) and a weight average molecular weight M_w of 410,000 was dissolved in a 7/3 (weight ratio) mixed solvent of N,N-dimethylacetamide (DMAc) and tripropylene glycol (TPG), to a copolymer concentration of 12 wt% at 25°C, to prepare a film-forming dope. The aforementioned nonwoven fabric was dip coated in the obtained dope, and then immersed in an aqueous solution with a 50 wt% solvent concentration for solidification and washed with water and dried to obtain a nonwoven fabric-reinforced separator. The mean film thickness of the separator was 25 μm and the basis weight was 18 g/m^2 . The Gurley value (JIS P8117) of this separator was 21 sec/100 cc. The q_m value was 0.40 mAh/cm^2 .

Separator C

A PET staple fiber with a fiber size of 0.33 dtex (product of Teijin Co., Ltd.) was used as the main fiber. A PET staple fiber with a fiber size of 0.22 dtex (product of Teijin Co., Ltd.) was used as the binder fiber. The main fiber and binder fiber were mixed in a proportion of 5:5, and a nonwoven fabric with a mean film thickness of 18 μm and a basis weight of 12 g/m^2 was

obtained by a wet sheeting method. The McMullin number of the nonwoven fabric was 6.3, and the (McMullin number x mean film thickness) product was 113.4. The Gurley value (JIS P8117) was 0.1 sec/100 cc or smaller.

5 A PVdF copolymer having a composition of vinylidene fluoride:hexafluoropropylene:chlorotrifluoroethylene = 92.2:4.4:3.4 (weight ratio) and a weight average molecular weight M_w of 410,000 was dissolved in a 7/3 (weight ratio) mixed solvent of N,N-dimethylacetamide
10 (DMAc) and tripropylene glycol (TPG), to a copolymer concentration of 12 wt% at 30°C, to prepare a film-forming dope. The aforementioned nonwoven fabric was dip coated in the obtained dope, and then immersed in an aqueous solution with a 50 wt% solvent concentration for
15 solidification and washed with water and dried to obtain a nonwoven fabric-reinforced separator. The mean film thickness of the separator was 24 μm and the basis weight was 17 g/m^2 . The Gurley value (JIS P8117) of this separator was 12 sec/100 cc. The q_m value was 0.79
20 mAh/cm^2 .

Separator D

A PET staple fiber with a fiber size of 0.33 dtex (product of Teijin Co., Ltd.) was used as the main fiber. A PET staple fiber with a fiber size of 0.22 dtex
25 (product of Teijin Co., Ltd.) was used as the binder fiber. The main fiber and the binder fiber were mixed in a proportion of 5:5, and a nonwoven fabric with a mean film thickness of 18 μm and a basis weight of 12 g/m^2 was obtained by a wet sheeting method. The McMullin number
30 of the nonwoven fabric was 6.3, and the (McMullin number x mean film thickness) product was 113.4. The Gurley value (JIS P8117) was 0.1 sec/100 cc or smaller.

A PVdF copolymer having a composition of vinylidene fluoride:hexafluoropropylene:chlorotrifluoroethylene =
35 92.2:4.4:3.4 (weight ratio) and a weight average molecular weight M_w of 410,000 was dissolved in a 7/3

(weight ratio) mixed solvent of N,N-dimethylacetamide (DMAc) and tripropylene glycol (TPG), to a copolymer concentration of 18 wt% at 90°C, to prepare a film-forming dope. The aforementioned nonwoven fabric was dip coated in the obtained dope, and then immersed in an aqueous solution with a 43 wt% solvent concentration for solidification and washed with water and dried to obtain a nonwoven fabric-reinforced separator. The mean film thickness of the separator was 25 μm and the basis weight was 21 g/m^2 . The Gurley value (JIS P8117) of this separator was 128 sec/100 cc. The qm value was 3.50 mAh/cm^2 .

Separator E

A fiber-opened glass cloth (No. E02E F 105B ST; product of Unitika Glass Fibers) having a basis weight of 17 g/m^2 , a mean film thickness of 18 μm and a yarn density of 95/95 (warp/weft)/25 mm was used as the base. The McMullin number of the glass cloth was 7.4, and the (McMullin number \times mean film thickness) product was 133. The Gurley value (JIS P8117) was 0.01 sec/100 cc.

A PVdF copolymer having a composition of vinylidene fluoride:hexafluoropropylene:chlorotrifluoroethylene = 92.2:4.4:3.4 (weight ratio) and a weight average molecular weight M_w of 410,000 was dissolved in a 7/3 (weight ratio) mixed solvent of N,N-dimethylacetamide (DMAc) and tripropylene glycol (TPG), to a copolymer concentration of 18 wt% at 90°C, to prepare a film-forming dope. The aforementioned glass cloth was dip coated in the obtained dope, and then immersed in an aqueous solution with a 43 wt% solvent concentration for solidification and washed with water and dried to obtain a glass cloth-reinforced separator. The mean film thickness of the separator was 24 μm and the basis weight was 24 g/m^2 . The Gurley value (JIS P8117) of this separator was 125 sec/100 cc. The qm value was 2.97 mAh/cm^2 .

Separator F

A separator with a mean film thickness of 22 μm and a basis weight of 21 g/m^2 was fabricated by the same fabrication method used for Separator E. The Gurley value (JIS P8117) of this separator was 104 sec/100 cc. The qm value was 2.03 mAh/cm^2 .

Separator G

The same nonwoven fabric of Separator A was used as the base. A film-forming dope was prepared by dissolving PVdF in N,N-dimethylacetamide (DMAc) to 10 wt%. The nonwoven fabric base material was dip coated in the obtained dope and then the solvent was dried to obtain a nonwoven fabric-reinforced separator. The mean film thickness of the separator was 25 μm , and the basis weight was 30 g/m^2 . The separator was so impermeable that the Gurley value was unmeasurable. The qm value was also unmeasurable.

The properties and base materials of Separators A to G obtained in the manner described above are summarized in Table 1.

Table 1

	Nonwoven fabric				Separator			
	Mean film thickness μm	Basis weight g/m^2	Gurley value sec/100 cc	McMullin number	Mean film thickness μm	Basis weight g/m^2	Gurley value sec/100 cc	qm mAh/cm^2
Separator A	17	14	<0.1	4.2	29	21	29	1.15
Separator B	20	12	<0.1	9.6	25	18	21	0.40
Separator C	18	12	<0.1	6.3	24	17	12	0.79
Separator D	18	12	<0.1	6.3	25	21	128	3.50
Separator E	17	18	<0.1	7.4	24	24	125	2.97
Separator F	17	18	<0.1	7.4	22	21	104	2.03
Separator G	17	14	<0.1	4.2	25	30	unmeasurable	unmeasurable

Electrodes

Positive electrode

A positive electrode paste was prepared using 89.5 parts by weight of a positive electrode active material powder, 4.5 parts by weight of acetylene black, and a 6

wt% solution of PVdF in N-methylpyrrolidone (NMP) with PVdF at a dry weight of 6 parts by weight. The resulting paste was coated and dried on a 20 μm -thick aluminum foil and then pressed to fabricate a positive electrode.

5 Lithium cobaltate (LiCoO_2), lithium nickelate (LiNiO_2), lithium manganate (LiMn_2O_4) and a mixture of LiNiO_2 and LiMn_2O_4 were used as positive electrode active materials. In the mixture of LiNiO_2 and LiMn_2O_4 , the
10 mixing ratios (weight ratios) were $\text{LiNiO}_2/\text{LiMn}_2\text{O}_4 = 3/7, 5/5, 7/3$. For each system, the positive electrode was fabricated to give the active substance weight W_p shown in Table 2.

Q_p

Q_p was determined by calculation from the
15 composition of LiCoO_2 , LiNiO_2 and LiMn_2O_4 . Specifically, these were Q_p (mAh/mg) = 0.278 (LiCoO_2), 0.278 (LiNiO_2) and 0.148 (LiMn_2O_4). For the mixed system ($\text{LiNiO}_2/\text{LiMn}_2\text{O}_4$), Q_p was determined by proportional calculation based on the weight ratio.

20 Q_{pr}

 A coin cell (CR2032) is fabricated using the positive electrode fabricated above and using a lithium foil as the counter electrode, after which constant current, constant voltage charging is carried out to 4.25
25 V at a current density of 0.5 mA/cm² (terminating at a current value of 10 $\mu\text{A}/\text{cm}^2$), and Q_{pr} can be determined by dividing the charging capacity ($Q_{pr}W_p$) during that time by the active substance weight (W_p). A polyolefin fine porous film (CELGARD #2400: product of Celgard Co., Ltd.)
30 was used for the separator in the cell, and 1 mol/dm³ $\text{LiPF}_6\text{EC}/\text{EMC}$ (3/7 weight ratio) was used as the electrolyte solution.

 The Q_pW_p and $Q_{pr}W_p$ values obtained by this method are shown in Table 2.

Table 2

	Active substance	Wp mg/cm ²	QpWp mAh/cm ²	QprWp mAh/cm ²
Co-1	LiCoO ₂	1.9	0.53	0.29
Co-2		9.1	2.53	1.41
Co-3		20.5	5.70	3.18
Ni-1	LiNiO ₂	4.4	1.23	0.88
Ni-2		7.1	1.96	1.41
Ni-3		15.9	4.42	3.18
Mn-1	LiMn ₂ O ₄	7.4	1.09	0.88
Mn-2		34.2	5.06	4.10
Mn-3		45.4	6.72	5.45
Ni/Mn-1	LiNiO ₂ /LiMn ₂ O ₄ = 3/7	22.0	4.11	3.17
Ni/Mn-2	LiNiO ₂ /LiMn ₂ O ₄ = 5/5	22.0	4.69	3.52
Ni/Mn-3	LiNiO ₂ /LiMn ₂ O ₄ = 7/3	22.0	5.26	3.87

5 Negative electrode

A negative electrode paste was prepared using 87 parts by weight of mesophase carbon microbeads (MCMB: product of Osaka Gas & Chemical Co.) powder, 3 parts by weight of acetylene black and a 6 wt% solution of PVdF in NMP with PVdF at a dry weight of 10 parts by weight, as the negative electrode active material. The resulting paste was coated and dried on an 18 μm-thick copper foil and then pressed to fabricate a negative electrode.

Negative electrodes were fabricated to give the active substance weights W_n shown in Table 3.

Q_n

A coin cell (CR2032) is fabricated using the negative electrode fabricated above and using a lithium foil as the counter electrode, after which constant current charging is carried out to 0 V at a current density of 0.1 mA/cm², and Q_n can be determined by dividing the charging capacity (Q_nW_n) during that time by the active substance weight (W_p). A polyolefin fine porous film (CELGARD #2400: product of Celgard Co., Ltd.) was used for the separator in the cell, and 1 mol/dm³ LiPF₆EC/EMC (3/7 weight ratio) was used as the electrolyte solution.

The Q_nW_n values obtained by this method are also

shown in Table 3.

Table 3

	Wn mg/cm ²	QnWn mAh/cm ²
N-1	0.9	0.30
N-2	2.7	0.90
N-3	4.6	1.50
N-4	9.7	3.20
N-5	12.4	4.10
N-6	16.7	5.50
N-7	10.9	3.60
N-8	11.8	3.90
N-9	6.5	2.14

5

Evaluation with coin cells

Fabrication of coin cells

Coin cells (CR2032) were fabricated in the following manner using each of the separators, positive electrodes and negative electrodes described above. After punching the positive electrode to $\phi 14$ mm, the negative electrode to $\phi 15$ mm and the separator to $\phi 16$ mm, they were stacked in the order: positive electrode/separator/negative electrode. The combination was immersed in the electrolyte solution and encapsulated in a battery case. The electrolyte solution used was 1 mol/dm³ LiPF₆EC/EMC (3/7 weight ratio).

The combinations of separator, positive electrode and negative electrode are shown in Fig. 4. Table 4 also shows the values for Q_{prWp} , q_m+WnQ_n , Q_pW_p and $1.3Q_pW_p$ calculated from the aforementioned measurement results.

Evaluation 1

Each fabricated coin cell was subjected to constant current, constant voltage charging carried out to 4.25 V at a current density of 0.2 C based on Q_{prWp} (charging terminating condition: 10 μ A/cm²), and then to constant current charging with a cutoff of 2.75 V at the same current density. The results are shown in Table 4. Cells which did not satisfy the charging termination condition due to an early overcharge-preventing function

were considered to have insufficient charging, and were evaluated as x. Cells which satisfied the charging termination condition and had an initial charge/discharge efficiency of 85% or greater were considered to be free of initial insufficient charging, and were evaluated as O. The results are shown in Table 4.

Evaluation 2

Each fabricated coin cell was subjected to overcharging by charging with an electric charge of 1000% with respect to QprWp, at a current density of 1C based on QprWp. The results are shown in Table 4. Cells with a constant voltage in a range below 5 V as shown in Fig. 1 were evaluated as ©. Cells which exhibited voltage oscillation as shown in Fig. 2 and were confirmed to have an overcharge-preventing function, but which had high oscillation exceeding 5 V or ceased oscillation during charging were evaluated as O. Cells in which absolutely no voltage oscillation was observed as shown in Fig. 3 and which exhibited about 5.5 V were evaluated as x. The results are shown in Table 4.

Table 4

No.	Separator	Positive electrode	Negative electrode	QprWp mAh/cm ²	qm+QnWn mAh/cm ²	QpWp mAh/cm ²	1.3QpWp mAh/cm ²	Evaluation 1	Evaluation 2
1	A	Co-1	N-1	0.29	1.45	0.53	0.69	O	x
2	A	Co-2	N-3	1.41	2.65	2.53	3.23	O	O
3	A	Co-3	N-4	3.18	4.35	5.70	7.41	O	⊗
4	B	Co-2	N-3	1.41	1.90	2.53	3.23	O	⊗
5	A	Ni-1	N-2	0.88	2.05	1.23	1.60	O	x
6	B	Ni-1	N-2	0.88	1.3	1.23	1.60	O	O
7	B	Ni-2	N-3	1.41	1.9	1.96	2.55	O	⊗
8	A	Ni-3	N-4	3.18	4.35	4.42	5.75	O	⊗
9	A	Mn-1	N-2	0.88	2.05	1.09	1.42	O	x
10	B	Mn-1	N-2	0.88	1.30	1.09	1.42	O	O
11	A	Mn-2	N-5	4.10	5.25	5.06	6.58	O	O
12	B	Mn-2	N-5	4.10	4.50	5.06	6.58	O	⊗
13	A	Mn-3	N-6	5.45	6.65	6.72	8.74	O	⊗
14	A	Ni/Mn-1	N-4	3.17	4.35	4.11	5.34	O	O
15	A	Ni/Mn-2	N-7	3.52	4.75	4.69	6.10	O	O
16	A	Ni/Mn-3	N-8	3.87	5.05	5.26	6.84	O	⊗
17	B	Ni/Mn-1	N-4	3.17	3.60	4.11	5.34	O	⊗
18	B	Mn-2	N-7	4.10	4.00	5.06	6.58	x	-
19	B	Mn-2	N-6	4.10	5.90	5.06	6.58	O	O
20	A	Mn-2	N-6	4.10	6.65	5.06	6.58	O	x
21	C	Co-3	N-3	3.18	2.29	5.70	7.41	x	-
22	D	Co-3	N-3	3.18	5.00	5.70	7.41	O	⊗
23	C	Ni-3	N-3	3.18	2.29	4.42	6.63	x	-
24	D	Ni-3	N-3	3.18	5.00	4.42	6.63	O	O
25	F	Ni-3	N-3	3.18	3.53	4.42	6.63	O	⊗
26	A	Ni/Mn-2	N-9	3.52	3.29	4.69	6.10	x	-
27	E	Ni/Mn-2	N-9	3.52	5.11	4.69	6.10	O	O
28	F	Ni/Mn-2	N-9	3.52	4.17	4.69	6.10	O	⊗
29	B	Co-3	N-4	3.18	3.60	5.70	7.14	O	⊗
30	G	Co-3	N-3	3.18	-	5.70	7.41	x	x

5 Table 4 shows that the cells satisfying the condition $Q_{pr}W_p < q_m + Q_nW_n$ exhibited no insufficient charging and were fully chargeable, whereas cells 18, 21, 23 and 26 which did not satisfy this condition were not capable of charging. However, even with such an

10 electrode construction, cells 22, 24, 25, 27 and 28 were able to avoid insufficient charging by changing the separator. A satisfactory overcharge-preventing function was also exhibited by cells satisfying the condition $q_m + Q_nW_n < Q_pW_p$, while cells satisfying the condition $Q_pW_p < q_m + Q_nW_n < 1.3Q_pW_p$ did not exhibit a complete

15 overcharge-preventing function but had significantly slowed decomposition of the electrolyte solution. In contrast, when $q_m + Q_nW_n > 1.3Q_pW_p$, the effect of the overcharge-preventing function could not be significantly

20 confirmed.

These results indicated that designing a cell to

satisfy inequality I above will yield a cell with no insufficient charging and a satisfactory overcharge-preventing function.

Also, it is self-evident from inequality I that when
5 $Q_{prWp} \leq Q_{nWn}$, a separator with a small q_m value increases the options for the positive electrode and thus facilitates the cell design, but this is also indicated by comparison between separator A and separator B.

In addition, comparison between separators A-C and
10 separators D-F indicates that the use of a separator with a large q_m value is preferred when $Q_{prWp} \geq Q_{nWn}$.

Separator G is a non-porous example, and in the case of this separator, the separator resistance was too high and did not exhibit the prescribed charging terminating
15 condition in the charging of Evaluation 1. Also, no overcharge-preventing function was exhibited in Evaluation 2. This indicates that a porous structure is essential, as represented by the Gurley value.

20 Industrial Applicability

As explained in detail above, a design satisfying inequality I effectively prevents overcharging and avoids insufficient charging and, therefore, allows a practical non-aqueous secondary battery to be provided which is
25 very safe with regard to overcharging.